The healing phase may further include at least one disilicide $MeSi_2$ where Me is a metal taken from groups 3 to 8 of the periodic classification of the elements (IUPAC standard).

The protective coating further includes a surface oxide film comprising the silica obtained by oxidizing the silicon and the silicides contained in the coating. The protective coating may further include an outer refractory layer. This may be a layer comprising at least one oxide such as a layer of silica, alumina, or zirconia glass, or a layer of a non-oxide ceramic such as silicon carbide (SIC) or silicon nitride (Si_3N_4) e.g. obtained by chemical vapor deposition.

The exceptional properties of the coating come from the particular compositions of the armature of the protective coating and of the eutectic uniformly distributed within the armature, in association with the generation of a surface oxide film. These properties include, in particular, the ability of the coating to provide protection against oxidation at surface temperatures that may be as high as at least 1850° C. and for parts having configurations and conditions of use that are most unfavorable. Performance is enhanced by the self-healing ability of the coating provided:

firstly, by the self-regenerating surface oxide film which is constituted essentially by amorphous silica doped with other components of the coating; and

secondly, by the eutectic which constitutes one of the structural elements of the coating and which, because of the respective compositions thereof, presents good adhesion to the other structural component of the coating that forms the armature; incidentally, it may be observed that this adhesion contributes to increasing the resistance to being swept away, since the armature retains the eutectic effectively even when the temperature exceeds the melting point of the latter.

The silicide-based armature of the coating remains homogeneous over a large temperature range and also has the ability to accumulate dopants, in particular niobium, tungsten, or tantalum coming from the underlying refractory material when the latter comprises an alloy of one of said elements.

In addition to its healing function, the eutectic makes it possible to accelerate the formation and the regeneration of the surface oxide film based on amorphous silica, in particular by facilitating migration, towards the surface, of silicon or other dopants that are included in the composition of the oxide film. Amongst such dopants, boron and yttrium contribute to facilitating the formation of a uniform surface film having improved protective ability. Boron and yttrium may be present in the coating in the form of YSi_2, titanium boride, and/or yttrium boride.

The performance of the anti-oxidation protection obtained by the invention makes it possible to envisage using refractory materials provided with said protection in applications such as hypersonic jet engines and aero-spacecraft where operation conditions can be very severe. Thus, without requiring complex and expensive cooling systems, it is possible to make parts for hypersonic jet engines or reaction chamber surface portions having sharp edges that are the site of intense localized thermal phenomena. In addition, it is also possible to make aerodynamic fairing elements for aero-spacecraft, such as the leading edges of the wings or the nose, in particular for space airplanes which are subjected to intense heat flows.

Another advantage of the invention is that the protective coating against oxidation can also be used for protecting refractory metal alloys, in particular alloys of niobium, of molybdenum, of tungsten, or of tantalum, and intermetallic compounds or alloys containing dispersed oxide phases, as well as for protecting refractory composite materials, in particular composite materials containing carbon such as carbon-carbon or carbon-SiC composites, or for providing anti-ignition protection or oxygen compatibility for metals such as aluminum, titanium, or nickel, as well as for their alloys and for their intermetallic compounds and alloys of the type TiAl, Ti_3Al, $TiAl_3$, NiAl, and Ni_3Al.

Another object of the invention is to provide a method enabling the above-defined anti-oxidation protective coating to be made.

According to the invention, such a method comprises the following steps:

preparing a mixture containing powders having the following composition in percentage by weight:

Ti: 15% to 40%

Mo: 5.0% to 30%

Cr: 0 to 8%

Y: 0% to 1.5%

B: 0% to 2.5%

Me: 0% to 10%, where Me is at least one metal other than Ti, and taken from groups 3 to 8 of the periodic classification of the elements

Si: balance needed in order to reach 100%

depositing the mixture on the surface of the material to be protected; and

performing at least one heat treatment at a temperature that is not less than the melting point of the eutectic of the coating.

Me is preferably selected from Mn, Fe, Co, and Ni.

The heat treatment comprises a first step under vacuum enabling the desired protective coating to be formed and enabling the coating to adhere to the surface of the material to be protected, and a second step performed in an oxidizing medium to enable an oxide film to be formed on the surface of the coating. The first step is performed at a temperature that is equal to or greater than the melting point of the eutectic, generally in a range of about 1300° C. to about 1600° C. The second step is performed in an oxidizing medium at a temperature lying in the range about 1200° C. to 1600° C., and preferably at least 1300° C. The second step, whose purpose is to achieve pre-oxidation, is not necessarily performed prior to the material being used, since it can take place on the first occasion that the material is put into operation.

A refractory outer layer may also be deposited on the surface of the material provided with the anti-oxidation coating. This outer layer may be formed by at least one refractory oxide, such as silica, alumina, or zirconia glass, or by a non-oxide ceramic, such as SiC or Si_3N_4, e.g. obtained by chemical vapor deposition.

A preferred composition in percentage by weight of the powder mixture is as follows:

Ti: about 30%

Mo: about 10%

Cr: about 0.2%

Y: about 0.5%

B: about 2%

Me: about 7%

Si: balance needed in order to reach 100%, in which composition Me is preferably iron.

Various techniques may be used for depositing the powder mixture on the surface of the refractory material.

The powder mixture is preferably put into suspension in a liquid, e.g. water, possibly also containing a dispersing wetting agent and/or a transient organic binder such as a cellulose varnish, a polymer of the polyvinyl alcohol type, etc., so as to make deposition possible by immersion, by